

Liquid and Solid Products from Liquid-Phase Pyrolysis of Softwood

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Published online: 15 June 2011
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Abstract Lignocellulosic feed is expected to contribute significantly to production of liquified and solid combustibles in future, because of the quantity and the variety of feed material. The aim of the project is the production of high-quality biochar and a liquid energy carrier in a non-aqueous hydrocarbon-based pyrolysis system. Therefore, the pyrolytic degradation properties of wood and its building blocks glucose, cellulose, hemicellulose, and lignin were investigated during liquid-phase pyrolysis conditions. The process was carried out in a semibatch reaction vessel under isothermal conditions at various temperatures between $T=350^{\circ}\text{C}$ and $T=390^{\circ}\text{C}$. Process pressure was ambient. For optimum heat transfer, pyrolysis was carried out in a liquid heat carrier phase which provides sufficient heat capacity and high heat conductivity for isothermal operation. The interaction between heat carrier, biomass, and biomass products in the liquid and vapor phases was investigated. Liquid-phase pyrolysis is an exothermic process which produces 25–28% liquid CHO

products. The heat of reaction is -864 ± 25 kJ/kg at $T=350^{\circ}\text{C}$. To quantify products of biogenous and fossil origin, liquid products were analyzed by elemental analysis, gas chromatography, and accelerated mass spectroscopy. Solid products were analyzed by elemental analysis, electron microscopy, and accelerated mass spectroscopy.

Keywords Biochar · Biomass to liquid · Liquid heat carrier · Liquid-phase pyrolysis

Abbreviations

GC	Gas chromatograph
FID	Flame ionization detector
MS	Mass spectrometer
BtL	Biomass to liquid
SimDis	Simulated distillation with GC
EDX	Energy-dispersive X-ray spectroscopy
AMS-C14	Accelerator mass spectroscopy to detect ^{14}C Atoms
IR	Infrared spectroscopy
SEM	Scanning electron microscopy
BDI	BDI-BioEnergy International AG
GPC	Gel permeation chromatography
ICP-OES	Inductively coupled plasma-optical emission spectroscopy

Introduction

Thirty percent of European Union energy consumption is needed for traffic and mobility, and 98% of these fuels are from fossil sources [1]. The European Union wants to reduce greenhouse gas emissions due to the European Directive 2009/28/EC by 20% and raise the percentage of renewable fuels up to 10% [2]. This policy and the strategies for sustainability open a wide range of possibilities for renewable resource fuels and combustibles all over

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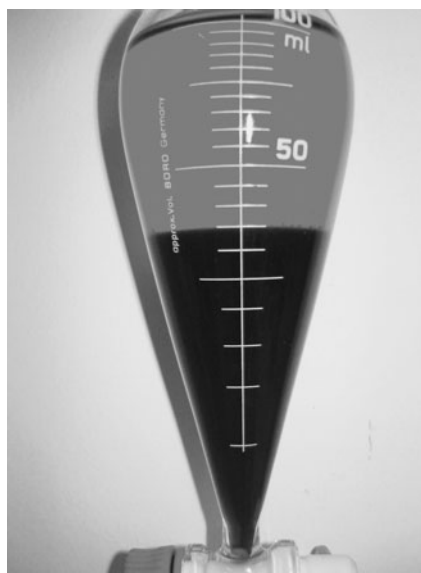


Fig. 1 Entrained heat carrier (*upper phase*) and biocrude oil (*lower phase*)

the world. BtL (biomass to liquid) can play a big role in conversion of biomass to fuels and energy carriers. Thermo-chemical conversion of biomass provides many applications in the value chain of fuels, electricity, and chemicals [3]. The number of different implementations

of BtL processes in Germany [4] and all over the world [3] is comparable with the variety of applications of BtL products [5]. Different systems concerning biomass pre-treatment, product conditioning and collecting, and reactor configuration are reported; different reactor systems have been investigated and proposed [6]. To avoid dust formation in the vapor phase and to provide high heat transfer during operation, the pyrolysis process was carried out in liquid phase. Neither does liquid-phase pyrolysis need high technical vapor biochar separation systems like in fluidized bed pyrolysis [7] nor does it demand high pressure reaction atmosphere like in hydrothermal carbonization reactors [8]. Liquid-phase pyrolysis is a KISS principle (keep it smart and simple) enabling high potential in production of biochar and biocrude oil [9].

Methods

Biomass Preparation

Feedstock for this study was bone-dry spruce wood to avoid formation of heterogeneous azeotropic mixtures of excess water and heat carrier biomass was dried for 24 h at 105°C. Pyrolysis of wood chips of different particle size of

Fig. 2 Schematic of the fed batch reactor

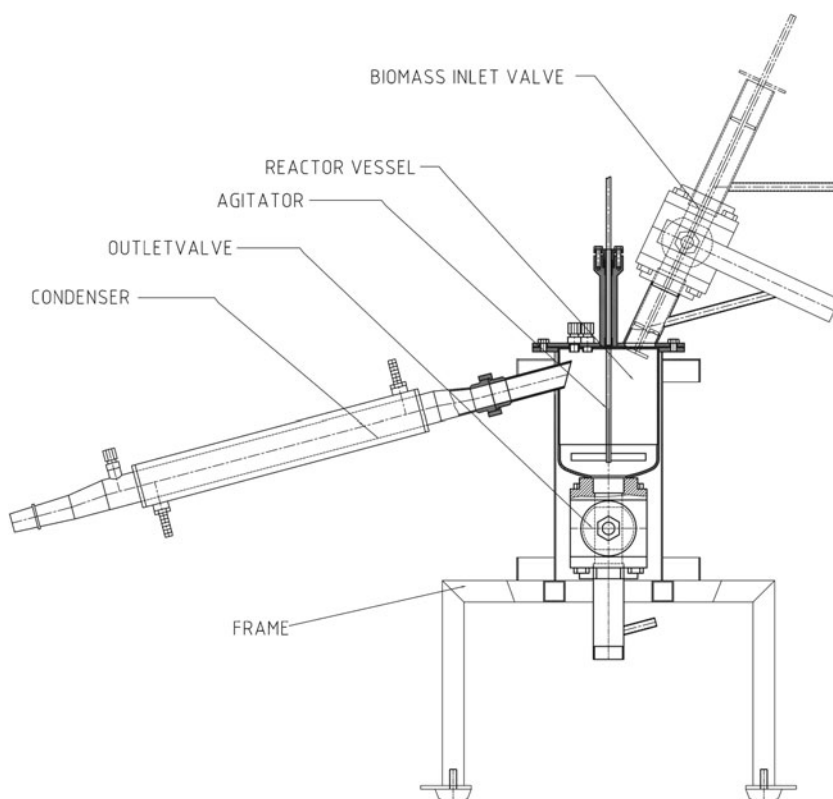
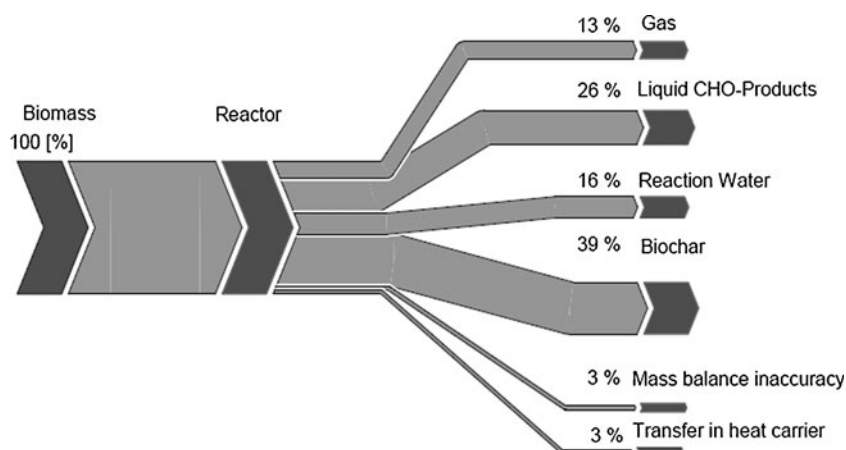


Fig. 3 Mass balance at $T=350^{\circ}\text{C}$



$10 \times 10 \times 10$ mm, $5 \times 5 \times 5$ mm and dust of 1–2 mm as well as dust of less than $630 \mu\text{m}$ was investigated.

System

Biomass was pyrolyzed in a liquid heat carrier at ambient pressure. The mass ratio was five parts of heat carrier to one part of biomass. Liquid heat carrier provides sufficient heat conductivity $\sim 0.100 \text{ W/mK}$ at $T=350^{\circ}\text{C}$ and high heat capacity of $\sim 2.4 \text{ kJ/kgK}$ at $T=350^{\circ}\text{C}$ for isothermal operation of semibatch pyrolysis. Heat carrier is a mixture of *n*-alkanes, with a boiling range between 410°C and 440°C . The total amount of heat carrier in the reaction vessel was 500 g. After 1 h and 20 min of preheating, the reactor temperature ($350\text{--}390^{\circ}\text{C}$) was obtained. The 16.6 g of biomass was then added six times every 5 min under nearly isothermal operation conditions. The temperature fluctuated $\pm 2^{\circ}\text{C}$ during metering of biomass. Products of liquid-phase pyrolysis are non-condensibles, biocrude oil, and biochar. During pyrolysis, the biocrude oil is entrained with heat carrier because of formation of heterogeneous azeotropes due to limited

miscibility of biocrude oil, water, and heat carrier, as shown in Fig. 1.

Reactor Design

The reactor was designed according to the needs of semibatch operation. The schematic is shown in Fig. 2. Biomass was added through a 40-mm ball-type inlet valve. The heat carrier was agitated by a stirrer at 150 rpm. All condensables were condensed in a water-cooled heat exchanger. Vapor temperature at the condenser outlet was set at $T \sim 15^{\circ}\text{C}$. Inert atmosphere was provided by two nitrogen purge lines. The temperature was controlled in the liquid heat carrier phase, in the vapor phase above the heat carrier at the condenser inlet, and at the end of the condenser, the temperature was recorded.

Analytics

The gas amount was measured by a red-y gas flow meter (Vögtlin). Gas composition was measured with a Hartmann+Braun advance Optima infrared and thermal conductivity

Fig. 4 Heat carrier mass balance at $T=350^{\circ}\text{C}$

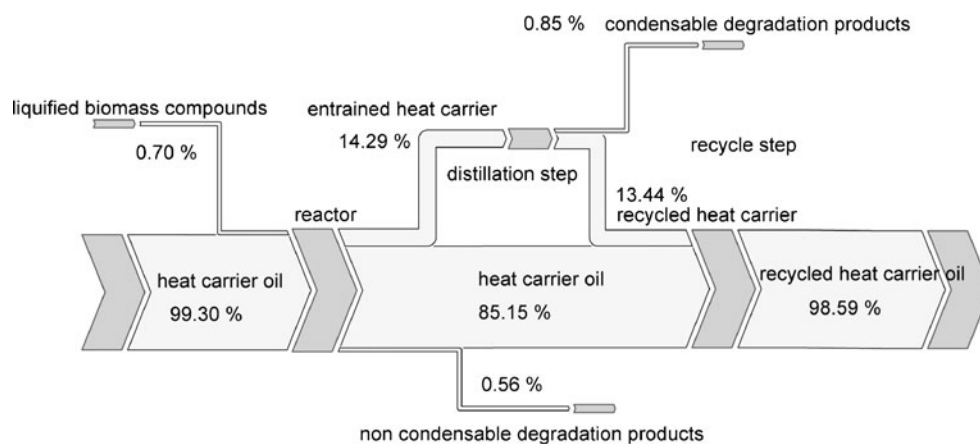
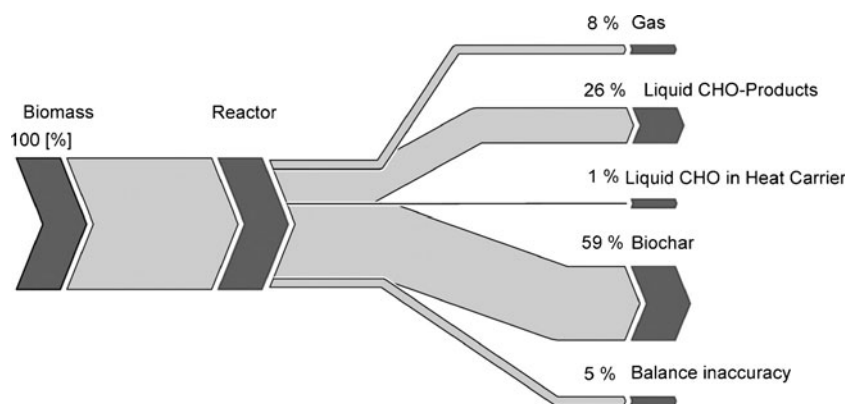


Fig. 5 Carbon balance at
T=350°C



measurement system and an AC Hi-Speed RGA GC (gas chromatograph) system (DIN 51666 approved), supplied by ASG Analytik-Service Gesellschaft.

All liquid and solid products and educts were characterized by elemental analysis with a Vario macro from Elementar Analysensysteme in Carbon, Nitrogen and Hydrogen mode. Liquid products were measured by gas chromatography-mass spectroscopy (GC-MS) 5890 Series from Hewlett Packard with a WCOT fused silica 30 m low bleed column. Heat carrier and entrained heat carrier were determined with a gas chromatograph-SimDis MXT 2887, 10 m column from Restek and Agilent 7890A GC. Water was measured with Titro Line Karl Fischer system from Schott. Molecule size distribution in biocrude oil was determined with gel permeation chromatography (GPC) on three separation columns with 500, 100, and 50 Å pore size from Polymer Standards Service (5 µm, 8×300 mm columns); signals were detected with a refractometer/viscometer from Viscotek. The pH was measured with a pH-meter from Orion. Heat carrier and biochar were separated by filtration in a first step and in a second step solid/liquid extraction with hexane in a Soxhlett apparatus for 24 h. Transfer of fossil carbon between the heat carrier and Biomass products was controlled with an AMS, following the ASTM-D6866 method supported by Beta Analytic Inc. Biochar was IR (infrared) characterized with a Bruker Hyperion by Graz

Center of Electron Microscopy. EDX (energy-dispersive X-ray spectroscopy) and SEM (scanning electron microscopy) photos were done with a FEI Quanta 200 ESEM and an EDAX Genesis EDX System by Graz Center of Electron microscopy. Element screening with ICP-OES and microwave-assisted sample decomposition was done by TU Graz Institute of Analytical Chemistry and Food Chemistry with a Spectro Ciros Vision EOP.

Results

Balances

During liquid-phase pyrolysis, lignocellulosic biomass is transferred into biocrude oil, which consists of water and liquid CHO products. Due to its polar nature, biocrude oil is nearly fully separable into its two main compounds, water and organics, by distillation. Biochar is the solid residue of liquid-phase pyrolysis. Figure 3 shows the mass balance of liquid-phase pyrolysis. The balance inaccuracy of 3 wt.% is mainly caused by dissolution of liquid-CHO products in the heat carrier which is evaporated. The heat carrier cycle is shown in

Table 1 Comparison between torrefaction, slow pyrolysis, and liquid-phase pyrolysis

	Torrefaction [16]	Slow pyrolysis [17]	Liquid phase pyrolysis
Temperature	300°C	300°C	350°C
Char [wt.%]	60.8	66.8	39
Liquid yield [wt.%]	28	28	42
Gas [wt.%]	11.2	5.2	13

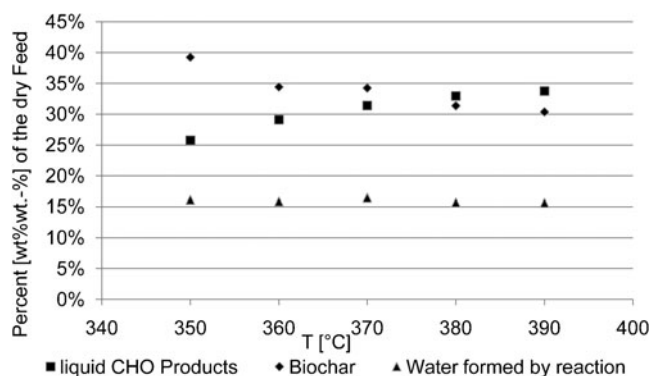


Fig. 6 Effect of temperature on liquid-phase pyrolysis

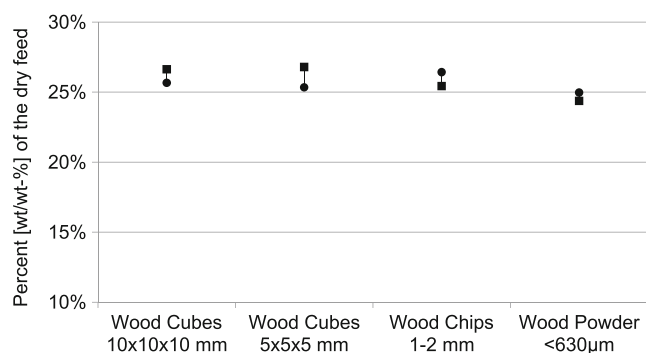


Fig. 7 Liquid CHO-product formation depending on particle size at $T=350^{\circ}\text{C}$

Fig. 4. The first step of the cycle is liquid-phase pyrolysis. During this process, about 3 wt.% of the biomass is dissolved in the heat carrier. Some heat carrier is evaporated because of formation of a heterogeneous azeotrope with water. About 1.4 wt.% of the heat carrier is cleaved to form non-condensable hydrocarbon volatiles and condensable hydrocarbons. These condensables mainly consist of alkanes and alkenes.

Degradation products dissolved in the heat carrier were identified to mainly consist of 2-methyl-furan, 2,5-dimethylfuran, 2-methoxyphenol, 2-methoxy-4-methylphenol, 4-ethyl-2-methoxyphenol, 2-methoxy-4-(2-propenyl)-phenol, 2-methoxy-4-propylphenol, 2-methoxy-4-(1-propenyl)-phenol. While 2-methyl-furan and 2,5-dimethylfuran originates in degradation carbohydrates, the majority of substances are formed through degradation of lignin sources like coniferyl alcohol.

Within the selected range of operation temperature, most carbon remains in the biochar, which is the target product of liquid-phase pyrolysis below $T=400^{\circ}\text{C}$. Based on the hydrocarbon balance, the transfer of biomass into the heat carrier does not exceed 3 wt.%. The carbon balance of biogeneously carbon in Fig. 5, deduced from C^{14} -analysis, confirms that, at least 1 wt.% of biogenous carbon feed dissolves in the heat carrier.

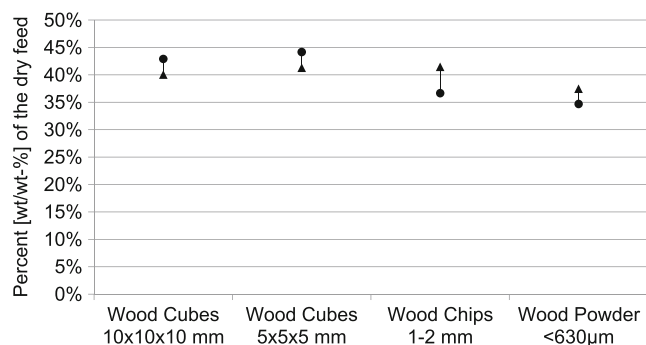


Fig. 8 Biochar formation depending on particle size at $T=350^{\circ}\text{C}$

Table 2 Composition of liquid-phase pyrolysis gas

Gas	[Vol.%]
Carbon dioxide	46
Carbon monoxide	33
Nitrogen	14
Methane	2
Oxygen	2
Hydrogen	0.5
Other volatile organic compounds	2

The transfer of biogeneously carbon into biochar makes liquid-phase pyrolysis more comparable with low-temperature processes like torrefaction and slow pyrolysis rather than fast or flash pyrolysis. Table 1 shows the product distribution of different pyrolysis processes.

Influence of Operation Temperature on Product Distribution

As expected [5], elevated temperature in the temperature range between 350°C and 390°C leads to rising liquefaction and decreasing amount of biochar as shown in Fig. 6. The carbon content of biochar as well as the amount of biocrude oil increases. Formation of water is not affected. Unfortunately, the heat carrier is not stable at temperatures above 350°C . The rate of carrier oil degradation rises exponentially with rising temperatures. The degradation mechanism follows strictly Arrhenius law with an activation energy = 171 kJ/mol and a frequency factor of $1.02 \times 10^9 \text{ (g} < \text{C}_{20})/(\text{gHC} \cdot \text{s})$.

Influence of Particle Size on Liquid-Phase Pyrolysis

Particle size of less than 10 mm shows a weak influence on formation of biochar and biocrude oil as well as on the composition of products. The effect of particle size on product distribution is shown in Figs. 7 and 8. Neither biocrude oil formation nor biochar formation

Table 3 Comparison of liquid-phase pyrolysis biocrude composition with literature [10]

Parameter	Liquid-phase pyrolysis	Fluidized bed reactor [10]
Yield (wt.%)	42	75
Water (%)	39	20
C (wt.%)	31.5	55
H (wt.%)	8.5	7
High heating value (MJ/kg)	11.6	20

Table 4 Inorganic load of biocrude

Element	[g/kg]
Ca	<0.15
K	<0.06
Na	<0.05
S	<0.15
Si	<0.13

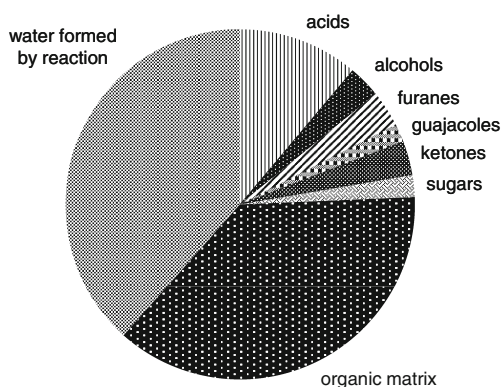
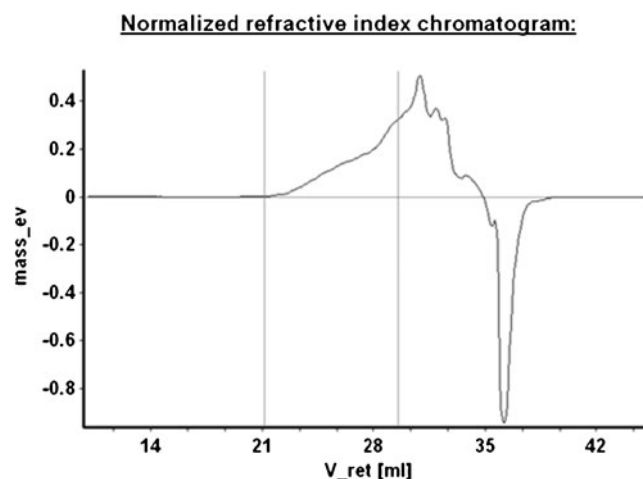
shows a significant dependence of the particle size. From these findings, one may conclude that the penetration length of the feed does not have an effect on the quality of products. Less biochar formation from small particles was rather caused by solid/liquid separation than by particle size.

Gaseous Products

Main components of the pyrolysis gas (the gaseous phase after separation of condensibles at $T=15^{\circ}\text{C}$) are carbon dioxide, carbon monoxide, nitrogen, and methane. A detailed list of the gas mixture is shown in Table 2. The source of nitrogen and oxygen in the system is biomass, which was deaerated with nitrogen before metering. The gas contains 2% of volatile organics with 0.5 vol.% of hydrocarbons with more than six carbon atoms, mainly from degradation of the heat carrier.

Liquid Products

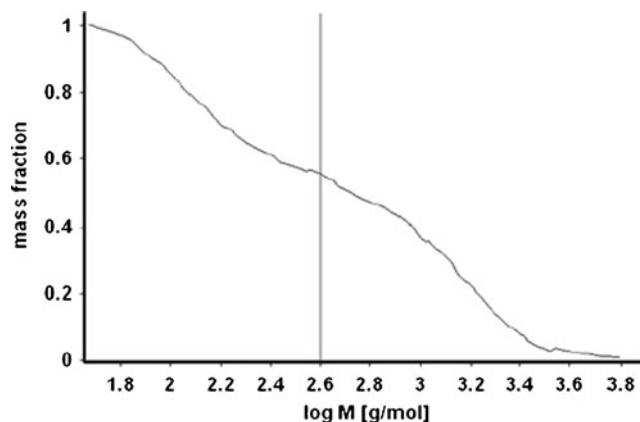
Liquid-phase pyrolysis biocrude oil is “light biocrude oil” compared with flash pyrolysis biocrude oil [10] in Table 3. As a result of preferred biochar formation, less biomass is transferred into liquid products, explaining elevated water content and low carbon contents.


Fig. 9 Biocrude oil main substance classes

Fig. 10 GPC chromatogram of liquid-phase pyrolysis-based biocrude oil

Biocrude oil from fluidized bed reactor pyrolysis is particle-loaded [11], a major disadvantage which is not observed in liquid-phase pyrolysis. All liquid products are completely ethanol-soluble. Without separation steps for ash and char particles, biocrude oil from flash pyrolysis can carry up to 500 ppm sodium and potassium and up to 600 ppm calcium [12]. In liquid-phase pyrolysis particulate matter is trapped in the liquid heat carrier inside the reactor, the reason for low inorganic compounds in the unfiltered and untreated biocrude oil, shown in Table 4.

Figure 9 shows the main constituent classes of biocrude oil, including the organic matrix, which is made up of oligomers [13]. GPC gives the approximate size of non GC-MS detectables. The molar mass of $M_w=400$ g/M compares well with carbohydrate di- and trimers, as shown in Figs. 10 and 11.

As shown in Fig. 7, biomass particle size does not affect formation of biocrude oil nor does it affect the composition


Fig. 11 Detail of GPC chromatogram with a M_w of 400 g/M

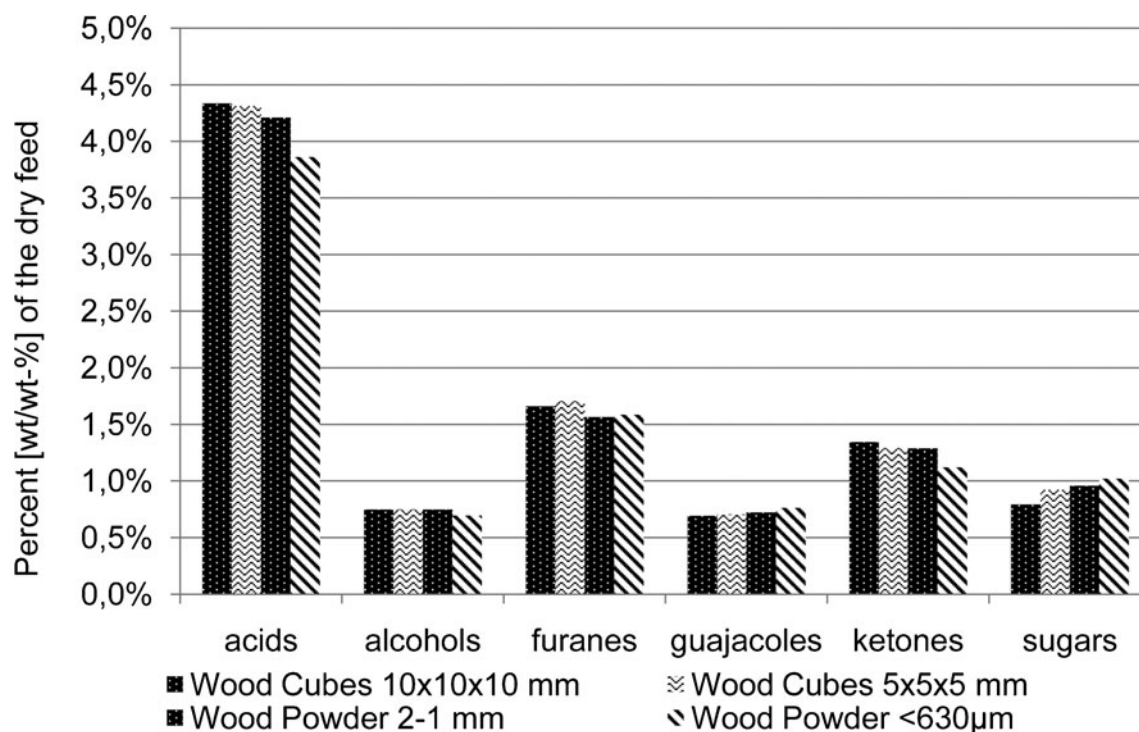


Fig. 12 Effect of particle size on composition of biocrude oil

of biocrude oil, as shown in Fig. 12. The total amount of acids decreases while the residual amount of sugar is observed when particle size is decreased.

Solid Product

As shown in Fig. 5, carbon is mainly transferred into biochar during liquid-phase pyrolysis. Table 5 shows the transfer of elements from feed to the solid residue during liquid-phase pyrolysis. An increase in temperature from $T=350^{\circ}\text{C}$ to $T=390^{\circ}\text{C}$ does not increase the relative amount of carbon in the residue. The total amount of biochar decreases with increasing temperature. During liquid-phase pyrolysis, the upper heating value of solids rises from 18.9 MJ/kg (biomass) to 27.3 MJ/kg (biochar) at

$T=350^{\circ}\text{C}$. The calorific value of biochar is comparable with the calorific value of bituminous coal [14].

The IR-spectrum of biochar and lignite tar pitch are well comparable. As shown in Fig. 13, structures and functional groups compare well with lignite tar pitch. Lower sulfur content improves significantly to mean quality of fossil coal. Bituminous coal has 1.5 wt.% sulfur, whereas the sulfur content of biochar is <0.02 wt.%.

SEM photographs in Figs. 14 and 15 show the structure of biochar from softwood after liquid-phase pyrolysis. While hemicelluloses and celluloses seemingly got pyrolyzed, the high-temperature-resistant lignin frame keeps almost stable. Toledano et al. showed that ultrafiltered lignin degrades at about 400°C during thermogravimetric analysis [15]. Below 400°C , lignin does not undergo liquefaction; shrinking and carbonization processes are observed. EDX analysis through the whole longitudinal section, shown in Fig. 16, showed the same C-to-O ratio at every point in the two-dimensional framework. From constant C-to-O ratio, constant pyrolysis of the whole particle is concluded.

Discussion

Liquid-phase pyrolysis is an adequate technology to produce high-value biochar and biocrude oil within a

Table 5 Elemental analysis of biomass and biochar

Compound	Biomass [wt.%]	Biochar [wt.%]
Carbon	49.5	75.3
Hydrogen	6.5	5.2
Nitrogen	0.1	0.5
Oxygen	43.8	18.5
Ash	0.2	0.6

Fig. 13 IR spectroscopy of biochar (black lower line) and lignite [18]

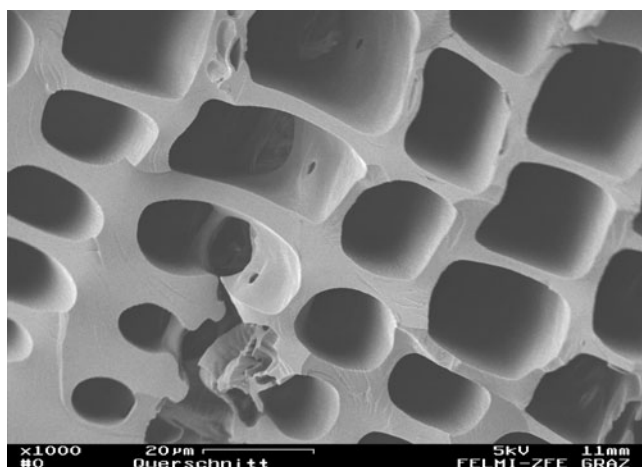
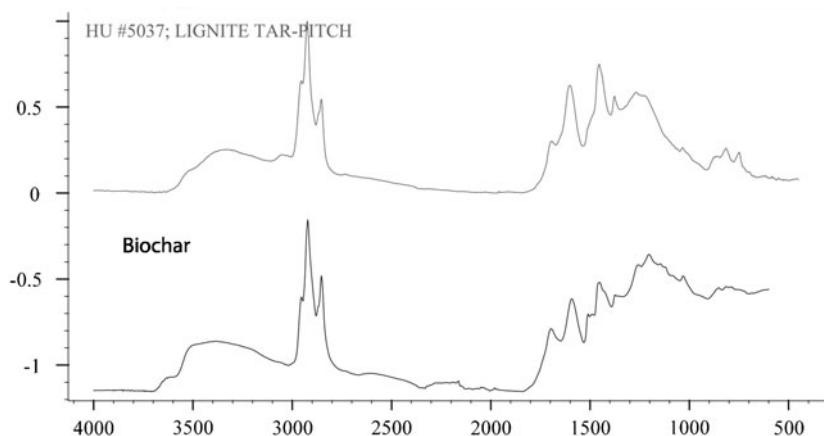


Fig. 14 Biochar cross section

short contact time and therefore cost of operation. Biochar formed through liquid-phase pyrolysis is a high-quality product with a broad field of industrial applications, including gasification, metallurgical applications, as well as production of value-added products in the chemical industry. Biocrude oil can be easily processed to obtain ready-for-market product quality. A major advantage of liquid-phase pyrolysis compared with fluidized bed processes is the simple energy management due to liquid-phase heat transfer, and dust-free operation. In comparison with high-temperature pyrolysis, the limitation of solids conversion according to the temperature limit of approximately $T=400^{\circ}\text{C}$ has to be mentioned.

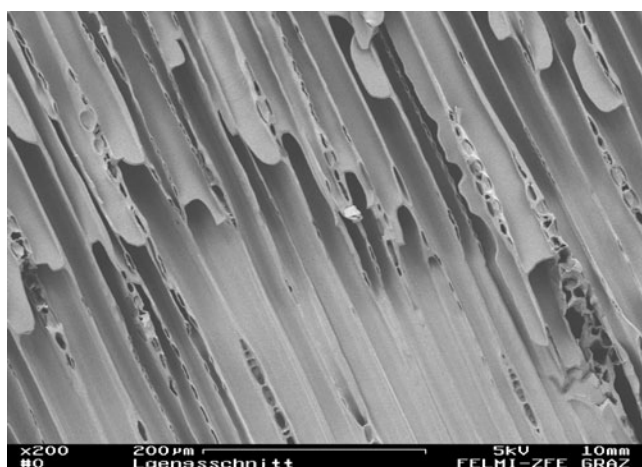


Fig. 15 Biochar longitudinal section structure

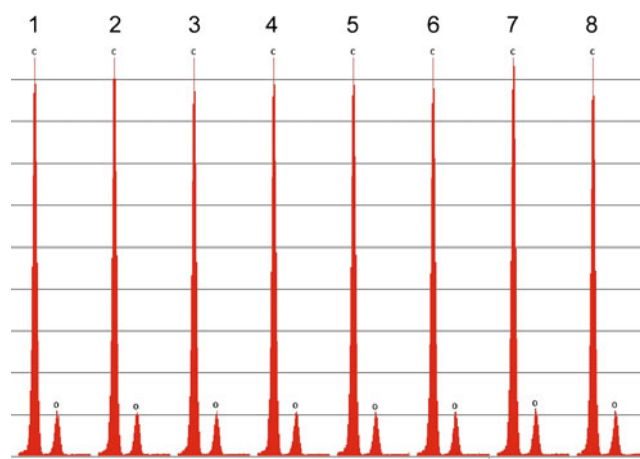


Fig. 16 EDX of liquid-phase pyrolysis biochar in a longitudinal section

Acknowledgment This project is supported by the Austrian climate- and-energy funds within the “Energy of the Future” program.

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